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Enhanced photovoltaic response of organic solar cell by singlet-to-triplet exciton conversion

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Ir complex was doped to conjugated polymers, and the photoinduced absorption of triplet excitons in host materials was examined. A greatly enhanced intersystem crossing rate was observed, despite the decrease in triplet exciton lifetime. The authors find that the steady-state triplet exciton population in host polymer would increase by an order of magnitude. Conjugated polymer/colloidal CdSe nanocrystal hybrid solar cells were fabricated and the effect of Ir-complex doping on photovoltaic response was studied. It was found that due to the enhanced singlet-to-triplet conversion, greatly enhanced photovoltaic response of these hybrid organic solar cells was observed. The results suggest that triplet solar cells may be achieved by doping conventional photovoltaic materials with transition-metal complexes. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2716209]

Organic solar cells have been under intensive investigation because of their promising cost effectiveness and environmental benignity. Due to strong Coulomb interaction in organic materials, photoexcited charged carriers quickly form singlet excitons.[1–3] These photogenerated excitons have to be dissociated before the charged carriers can be eventually collected by the electrodes. Donor-acceptor-type heterojunctions were demonstrated to be effective for exciton dissociation.[4–6] To achieve high power conversion efficiency, long exciton diffusion length is required for donor-acceptor heterojunction to affect efficient charge separation. The photogenerated singlet excitons are, however, prone to decay radiatively because of their dipole-allowed spin state, leading to a very short exciton lifetime and thus short diffusion length. The diffusion length of singlet excitons in most photovoltaic materials is usually 5–10 nm,[7,8] much shorter than the absorption depth required for efficient light absorption. Although special solar cell structures, such as bulk heterojunction, can be used to achieve both efficient light absorption and charge separation, they impede severely charge transport and are difficult to use in multilayered structures. Compared with singlet excitons, the radiative decay of triplet excitons is dipole forbidden. The lifetime of triplet excitons is therefore much longer than singlet excitons.[9,10] Consequently it is advantageous to convert the photogenerated singlet excitons to triplet excitons for efficient solar energy harvesting. Solar cells based on triplet material have been proposed;[11] however, the triplet organic material employed has low charged carrier mobilities, and there is no direct measurement of the triplet exciton population. Low carrier mobilities will decrease charge transport and carrier collection efficiency, leading to a compromised photovoltaic performance. In this letter, instead of using triplet exciton materials, the singlet-to-triplet exciton conversion is achieved by doping conventional conjugated polymers with transition-metal complex and the triplet exciton population is characterized spectroscopically. We found that upon blending Ir complex, the intersystem crossing (ISC) rate in polyfluorene can be greatly enhanced and the steady-state triplet exciton population would increase by an order of magnitude, leading to a greatly improved photovoltaic response.

Although most conjugated polymer related solar cells employ regio regular poly(3-hexylthiophene) (P3HT) because of its higher carrier mobilities, the photoinduced absorption (PA) signal of triplet excitons overlaps with polaron peak in regioregular P3HT, and precise determination of the triplet PA is difficult. We therefore chose poly(9,9-dioctylfluorenyl-2,7-diyl) end capped with dimethylphenyl (PFO) for PA measurements. Iridium (III) tris[2-(4-totyl)pyridinato-N,C2] [Ir(mppy)$_3$] is added to enhance the singlet-to-triplet exciton conversion. The Ir-complex phosphor is blended into the polymer with various wt % in toulene. Both the PFO and Ir(mppy)$_3$ were purchased from American Dye Source. The film thickness for PA experiments is 750±50 Å. For comparison with photovoltaic response, organic/inorganic hybrid solar cells[12,13] made of Ir-complex doped PFO/CdSe and Ir-complex doped P3HT/CdSe are used. With these organic/inorganic hybrid structures, the Ir complex is expected to be confined in the conjugated polymers, and the effect of Ir-complex doping on conjugated polymers alone can be studied. The device structure is conventional and consists of indium tin oxide/poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (50 nm)/blended layer (90 nm)/Al. P3HT was purchased from Aldrich Inc. Colloidal CdSe nanodots are synthesized from CdO and and Se precursors with trioctylphosphine ox-

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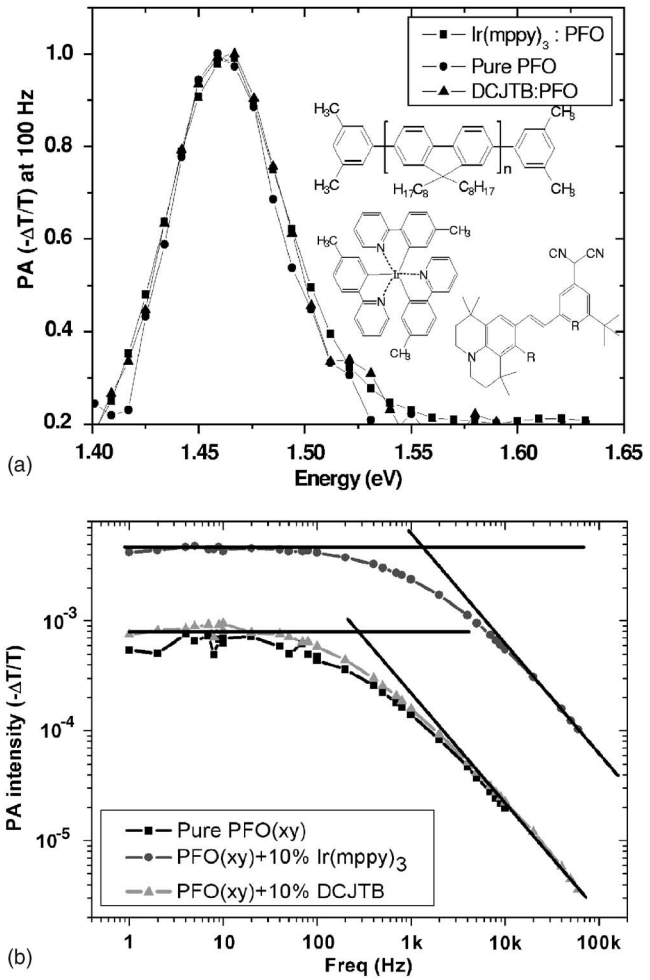

FIG. 1. (a) PA spectra of PFO without and with doping of $Ir(mppy)_3$ and DCJTB. The PA spectrum is taken at 100 K with modulation frequency of 100 Hz. (b) Frequency-dependent PA signal of pure PFO and PFO doped with $Ir(mppy)_3$ and DCJTB. While the doping with DCJTB shows no effects, the doping with $Ir(mppy)_3$ leads to decrease in triplet exciton lifetime from 0.4 to 0.14 ms and ten times increase in the steady-state triplet exciton population. The inset in (a) are the chemical structures of PFO, $Ir(mppy)_3$, and DCJTB.

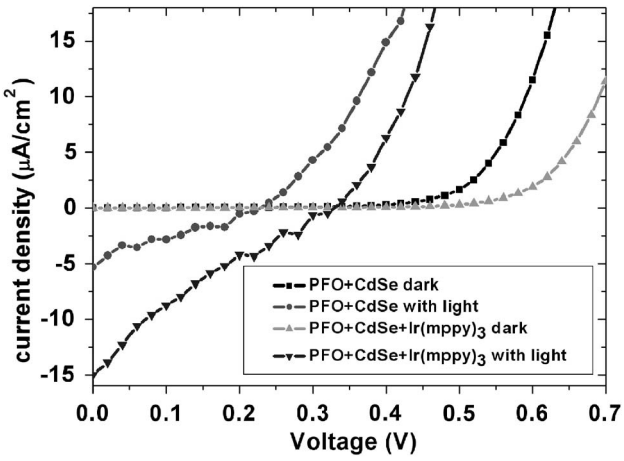

FIG. 2. Dark and photovoltaic responses of hybrid solar cells made from PFO/CdSe with and without $Ir(mppy)_3$, showing 200% increase in short-circuit current and 50% increase in open-circuit voltage upon doping of $Ir(mppy)_3$.

ide (TOPO) surfactant. The synthesized CdSe nanocrystal is purified in methane and ethane, and the TOPO surfactant is removed later by pyridine. Chloroform is used as solvent for the blended layers in the hybrid solar cells, which consists of 0.2 wt % (1.8 wt %) of conjugated polymer (CdSe) when there is no Ir-complex doping. The concentration dependence of singlet-to-triplet conversion on Ir complexes has been investigated, and the ISC was found to be greatly enhanced for doping more than 5%.[14] In this experiment, an additional 0.02 wt % $Ir(mppy)_3$ is added to the solvent, which consistutes 10 wt % as compared to the polymers.

The PA signal at 1.45 eV for triplet excitons in PFO is measured.[15] A 405 nm diode laser is used as the excitation source. At this wavelength, the absorption of PFO is high, whereas the absorption of $Ir(mppy)_3$ is weak. Although not shown here, the PA of triplet exciton in PFO was found be weak at room temperature. The PA measurement were therefore performed at 100 K to achieve higher signal-to-noise ratio. The room-temperature photovoltaic response is also measured with the diode laser of 405 nm wavelength at a power of 2.3 mW/cm^2. From the rate equation, the PA magnitude is proportional to $\tau_T/\sqrt{\tau_T^2\omega^2+1}$, where τ_T is the triplet exciton lifetime and $\omega=2\pi f$ is the angular modulation frequency of optical pumping.[15,16] The triplet exciton lifetime τ_T can be determined by the crossover frequency $1/2\pi\tau_T$ of the lower frequency limit, for which $\omega\tau_T \ll 1$, and higher frequency limit for which $\omega\tau_T \gg 1$. Moreover, the dc component of PA is directly correlated to the steady-state population of triplet excitons.

Figure 1(a) shows the PA spectrum taken at 100 Hz modulation. It can be seen that the PA of triplet exciton at 1.45 eV is not affected by doping with either $Ir(mppy)_3$ or organic fluorescent dye 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB), the latter of which does not have strong spin-orbital coupling, and was added as comparison. From Fig. 1(b), we observe that while the triplet exciton lifetime τ_T and steady-state population are not affected by the doping of DCJTB, τ_T decreases from 0.4 ms for pure PFO to 0.14 ms, and the steady-state triplet exciton population is increased by an order of magnitude upon doping of 10 wt % $Ir(mppy)_3$. This implies that the large effects of $Ir(mppy)_3$ result from the heavy-metal spin-orbital coupling. The decrease in triplet exciton lifetime is attributed to the enhanced radiative decay and the energy transfer to $Ir(mppy)_3$ by Dexter energy transfer. Since the steady-state population of triplet excitons is related to the product of their lifetime by their generation rate from ISC, the increase in the PFO triplet exciton population must be due to an even greater enhancement of ISC rate in PFO upon doping with $Ir(mppy)_3$. It is remarkable that the Ir complex has a tremendous effect on the ISC of the host polymer, besides their possible roles as carrier traps. Therefore, it may be possible to dope conjugated polymers of high carrier mobilities for enhanced singlet-to-triplet exciton conversion while maintaining reasonably high charge carrier mobilities.

The dark and photovoltaic responses of hybrid solar cells made from blended PFO/CdSe with and without $Ir(mppy)_3$ doping are shown in Fig. 2. It is observed that as the dark current decreases, the short-circuit current increases by 200% with the addition of 10 wt % $Ir(mppy)_3$. The decrease in dark current is attributed to the presence of $Ir(mppy)_3$ trapping sites for charge transport and the increase in short-circuit current, the greatly enhanced long-lived triplet excitons. It is

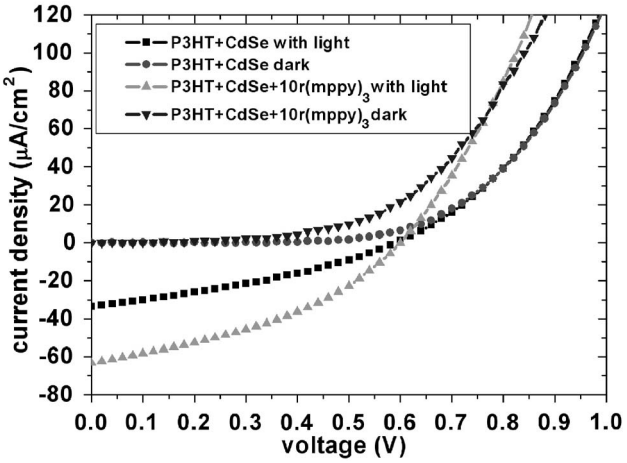

FIG. 3. Dark and photovoltaic responses of hybrid solar cells made from P3HT/CdSe with and without $Ir(mppy)_3$, showing 100% increase in short-circuit current upon doping of $Ir(mppy)_3$.

also notable that the open-circuit voltage is increased by 50%. The increase in both short-circuit current and open-circuit voltages leads to much enhanced photovoltaic response for the PFO/CdSe hybrid solar cells with addition of $Ir(mppy)_3$.

Figure 3 shows the dark and photovoltaic responses of hybrid solar cells made from blended P3HT/CdSe with and without $Ir(mppy)_3$ doping. Again, the short-circuit current is found to increase by 100% upon the addition of 10 wt % $Ir(mppy)_3$, revealing a much increased population of triplet excitons. The dark current is found to increase with Ir-complex doping. It is to note that, in contrast to the case of PFO, $Ir(mppy)_3$, with electron affinity (EA) and ionization potential (IP) being 2.4 eV and 5.4 eV respectively, would not affect charge trapping in P3HT (EA=3.0 eV, IP =5.1 eV). By reducing the formation of short-lived singlet excitons from injected charge carriers, the enhanced ISC with $Ir(mppy)_3$ doping may thus lead to increase in dark current. It also suggests that the carrier mobilities in P3HT may not suffer much with Ir-complex doping. Although we are not able to measure the triplet PA signal from P3HT blended with $Ir(mppy)_3$ directly, we expect similar enhancement of ISC and thus singlet-to-triplet exciton conversion. The enhancement of photovoltaic response of P3HT/CdSe hybrid solar cells is therefore expected. It is also noteworthy that $Ir(mppy)_3$ is highly phosphorescent and may not be the optimal choice for solar energy harvesting. Nevertheless, our results clearly suggest the possibility of enhanced singlet-to-triplet exciton conversion by doping conventional photovoltaic materials with transition-metal complexes. A large variety of possible combinations is therefore available to optimize the solar cell design. Moreover, with this approach, multilayered organic solar cells that make use of long-lived triplet excitons may be feasible.

To sum up, we analyzed the PA signal of triplet excitons in PFO and found an order of magnitude increase in the steady-state triplet exciton population upon the addition of $Ir(mppy)_3$. This increase in triplet exciton population is attributed to the increase in ISC rate by $Ir(mppy)_3$. Hybrid solar cells made of PFO/CdSe and P3HT/CdSe with the addition of $Ir(mppy)_3$ were fabricated, and great enhancement in their photovoltaic response was observed.

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